Journal of Energy Technologies and Policy
ISSN 2224-3232 (Paper) ISSN 2225-0573 (Online)
Vol.4, No.4, 2014
www.iiste.org

Thermal Characterization of Pine Sawdust as Energy Source Feedstock

Zephania Chaula[1*] Mahir Said[2] Geoffrey John[1]

1. Department of Sustainable Energy Science and Engineering, The Nelson Mandela African Institution of Science and Technology, PO box 447, Arusha, Tanzania
2. Department of Mechanical and Industrial Engineering, University of Dar-es-Salaam, PO box 35131, Dar-es-Salaam, Tanzania

* E-mail of the corresponding author: chaulaz@nm-aist.ac.tz

The authors wish to thank The Nelson Mandela African Institution of Science, Technology, and Commission for Science and Technology, Tanzania for their generous financial and materials support rendered to allow this research work to be conducted. The University of Dar-es-Salaam, Energy laboratories, staff and students are highly acknowledged towards this research.

Abstract

Pine sawdust was analyzed for thermal chemical conversion such as combustion, torrefaction, pyrolysis and gasification. The methods used to analyze involved performing proximate analysis, ultimate analysis, heating value and thermal decomposition for determining the biomass characteristics. Based on elemental composition, the pine sawdust exhibited lower energy content of 15.01 MJ/kg than bituminous coal that has about 31.8 MJ /kg. The kinetic parameters of pine sawdust described the individual component decomposition; the easiest component to decompose is hemicelluloses followed by cellulose and lignin. The heat released during thermal degradation of pine sawdust was -4380 J/g under inert condition, this shows pine sawdust potential for production of energy during combustion.

Keywords: Thermogravimentry, Kinetics, Pine Sawdust, Differential Scanning Calorimetry

1. Introduction

In most wood using industries the common wood by-products that are used as a source of energy are sawdust, deformed stem and slabs (Rose et al., 2009). Wood biomass boilers are highly suited to the forest product industry, here the fuel is generated on-site and where both process steam and electricity or shaft power are required (Miller and Tillman 2008). The estimated potential of sawdust in Africa is 822 PJ/year (Stecher et al., 2013). Tanzania is estimated to have a total biomass potential from plantation forests residue of over 205,400 m3 (Ngeleja, 2003; Kamwenda and Mkeya 2000). The biomass could be used as alternative source of energy if its thermal characteristics are known. The characteristics that define biomass as energy resource are proximate, ultimate and thermo-gravimetric analysis among others.

The proximate and ultimate analysis describe whether the biomass sample is combustible or not and if combustible the amount of volatile is important, since it describes type of the flame produced during combustion. The biomass that contain high volatile burn with a thick and bright flame, while those with less volatile burn with a dim and transparent flame. Unsuitable material during combustion is ash. Since high ash, content leads to fouling problems especially if the ash is high in metals alkali (Clarke and Petro, 2011).

Renewability, flexibility, and local availability of sawdust resources in many places make sawdust an attractive option for various applications. Potential applications for sawdust include firewood, briquettes, and wood pellets for home and institutional heating. In the production of heat and power, biomass can be used alone or co-fired. Because the existing power plant equipment can be used without major modifications, cofiring is far less expensive than building a new biomass power plant. Compared to the coal, biomass reduces SO_2, NO_X, and certain other air emissions (Lempp, 2013).

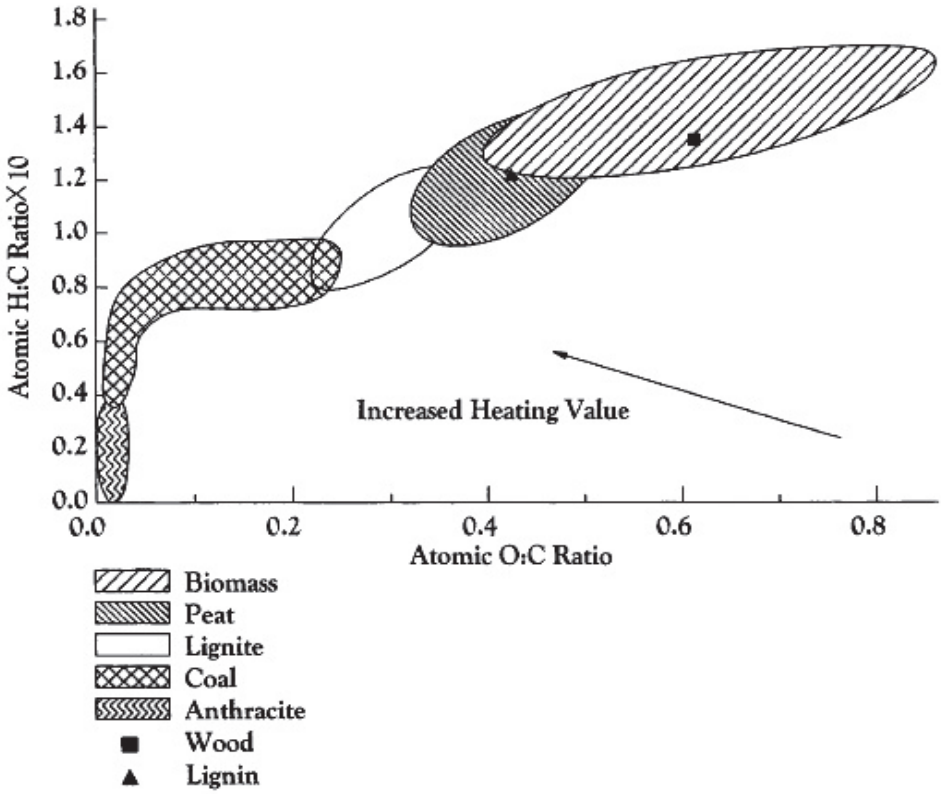

Figure 1 Van Krevelen Diagram for Various Solid Fuels (MacKentry, 2002)

The parameters that are related to the energy content of a solid fuel are the ratios of atomic oxygen to carbon (O/C) and atomic hydrogen to carbon (H/C) in a given solid fuel. High content in oxygen determines low energy content. Thus, the higher the O/C ratio the lower the energy content will be. The van Krevelen diagram (Figure 1) gives the relation between O/C and H/C for different solid fuels. From the diagram, it can be seen that high proportion of oxygen reduces the energy content of a given solid fuel. Due to this fact, anthracite and coals are solid fuels with the highest energy content, while the biomass is a solid fuel with low energy content (MacKentry, 2002). A typical biomass has a heating value of about 18-20 MJ/kg while a bituminous coal has a heating value between 24.5-31.8 MJ/kg (Chmielniak and Sciazko, 2003; Kurkova et al., 2003).

Due to chemical reactions, taking place during thermal degradation of biomass kinetic parameters such as activation energy, pre-exponential factor and reaction constant are estimated by deployed the thermogravimetric analysis (TGA). The kinetic parameters are used to predict product yield of biomass materials during pyrolysis; therefore, it can give an indication of the potential of the biomass material as a fuel.

2. Methodology

Pine sawdust samples for this study were obtained from Sanya Juu forest, West Kilimanjaro in Tanzania. The samples were sun dried for six hours and kept in an airtight bag to avoid absorption of moisture. The pine sawdust samples were ground to particle size less than 1mm and analysed for proximate, ultimate and thermal degradation.

The standard method deployed for proximate analysis was BS 1016: PART 1, 3:1973. The pine sample elemental composition including Carbon, Hydrogen and Oxygen were evaluated using correlations in accordance to the method of Parikh et al. (2007). Other elements were analyzed by deployment of Atomic Absorption Spectrometry (AAS).

The thermo-gravimetric analyzer model NETZSCH STA 409 PC Luxx was used to study the mass loss of pine sawdust, when heated under inert condition. Before thermo-gravimetric analysis, the sawdust sample was oven dried at 378 K (105oC) to a constant weight for removing the moisture. A purge gas, pure Nitrogen, was supplied to remove air in the thermo-gravimetric analyzer in order to avoid combustion during the experiment.

Subsequently, a 30 mg sample was put in the thermo-gravimetric analyzer, the heating medium being nitrogen with a flow rate of 60 ml/min at heating rates of 5, 10, 20, 40 K/min. The samples were heated from a room temperature to 1273 K (1000 °C).

The results obtained from the thermo gravimetric analyzer are curves of TG and DSC against temperature and time. The TG curves were used to derive DTG curves, which were used to determine kinetic parameters by Kissinger's method. The kinetic parameters were calculated from the Arrhenius Equation (1).

$$k = A\exp(-E_a / RT) \tag{1}$$

$$dx/dt = Af(x)\exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

$$x = \frac{(w_0 - w)}{(w_0 - w_\infty)} \tag{3}$$

Where k is the rate constant, which depends on temperature, A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant, T is the absolute temperature, f(x) is the algebraic function depending on the reaction mechanism and x is the reacted fraction as shown in Equation (3).

When the temperature rise at a constant heating rate (β), Equation 4, the differentiation of Equation 2 results into Equation 5.

$$\beta = \frac{dT}{dt} \tag{4}$$

$$\frac{d^2x}{dt^2} = \left\{\frac{E_a\beta}{RT^2} + Af'(x)\exp\left(-E_a / RT\right)\right\}\frac{dx}{dt} \tag{5}$$

The maximum rate occurs at a temperature Tpeak. When the rate of degradation reaches maximum, Equation 5 becomes equal to zero and the approximations from the calculations yield Equation 6.

$$\ln\left(\frac{\beta}{T_{peak}^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \left(\frac{E_a}{RT_{peak}}\right) \tag{6}$$

Equation 6 is a straight line graph, of $\ln\left(\beta / T_{peak}^2\right)$ v/s $1/T_{peak}$, The line slope is E_a / R and the intercept on the vertical axis is an $\ln(AR / E_a)$, which are used to determined Ea and A.

The fractional pyrolysis of biomass component is obtained by taking the ratio of the change of mass at time t and total reactive mass as shown in Equation 3.

3. Results and Discussion

The parameters that influence the energy content of solid fuels are oxygen to carbon ratio and hydrogen to carbon ratio as shown in Van Krevelen diagram (Figure 1). The elemental composition of pine sawdust gives the atomic ratio of oxygen to carbon, which is different to that of fossil fuels. Coal is one of solid fossil fuel and its maximum oxygen to carbon ratio is about 0.2 (Tsamba, 2008; Sami et al., 2001) with a heating value of 30 MJ/kg, while the pine sawdust has a higher atomic ratio of 0.89, and a heating value of 15.10 MJ/kg.

Table 1. Characterization of pine sawdust

Proximate Analysis, dry basis (%wt)		Ash composition (%wt)		Higher Heating Value (HHV) MJ/kg
Moisture	16.44	Sodium	90.90	
Volatile Matter	81.03	Sulfur	3.56	
Fixed Carbon	18.60	Potassium	3.23	
Ash	0.37	Iron	0.76	15.10
Ultimate Analysis (%wt)		Chlorine	0.40	
Carbon	48.62	Phosphorus	0.38	
Hydrogen	5.79	Chromium	0.35	
Oxygen	43.20	Lead	0.30	
Nitrogen	2.39	Copper	0.06	
“H:C” Ratio	0.12	Zinc	0.04	
“O:C” Ratio	0.89	Manganese	0.03	

The properties of pine sawdust are listed in Table 1. The analysis findings shows that pine sawdust have a heating value of 15.01 MJ/kg with high content of volatiles (81.03 %wt), carbon (48.62 %wt), hydrogen (5.79 %wt) and oxygen (43.2 %wt). The relative content of nitrogen, sulphur, and chlorine is marginal. This is a typical composition of biomass (Criado and Ortega 1986). The presence of chlorine (Cl) and sulphur (S) in pine sawdust are not desirable in combustion properties. Chlorine and sulphur are the major contributing factor to ash formation as they facilitate the mobility of inorganic compounds from the fuel to surfaces where they form the corrosive compounds (Wilson, 2010).

The results revealed that the volatile matter and fixed carbon of biomass are 81.03 %wt and 18.60 %wt respectively, while that of coal are 35 %wt and 57 %wt respectively (McKentry, 2002). The significance of volatile matter and fixed carbon contents is that they provide a measure of the ease with which the fuel has ignited and subsequently gasified, or oxidized. Due to that biomass can be utilized as an energy source.

The utilization of biomass for power and heat generation is facing some technical challenges of ash deposition and corrosion. The ash of biomass contains high level of alkali metals particularly sodium, which is about 90 %wt. The chlorine and sulphur concentration are in small amount about 3 %wt, which they cause the deposited ash to be corrosive, which is more severe than that of coal (Shao et al., 2012). Miller and Tillman (2008) reported that high number of boilers that use biomass as a fuel experience significant deposition due to either slagging (in the furnace zone) or as fouling. The problem becomes worse when chlorine is presented resulting in the formation of alkali chlorides.

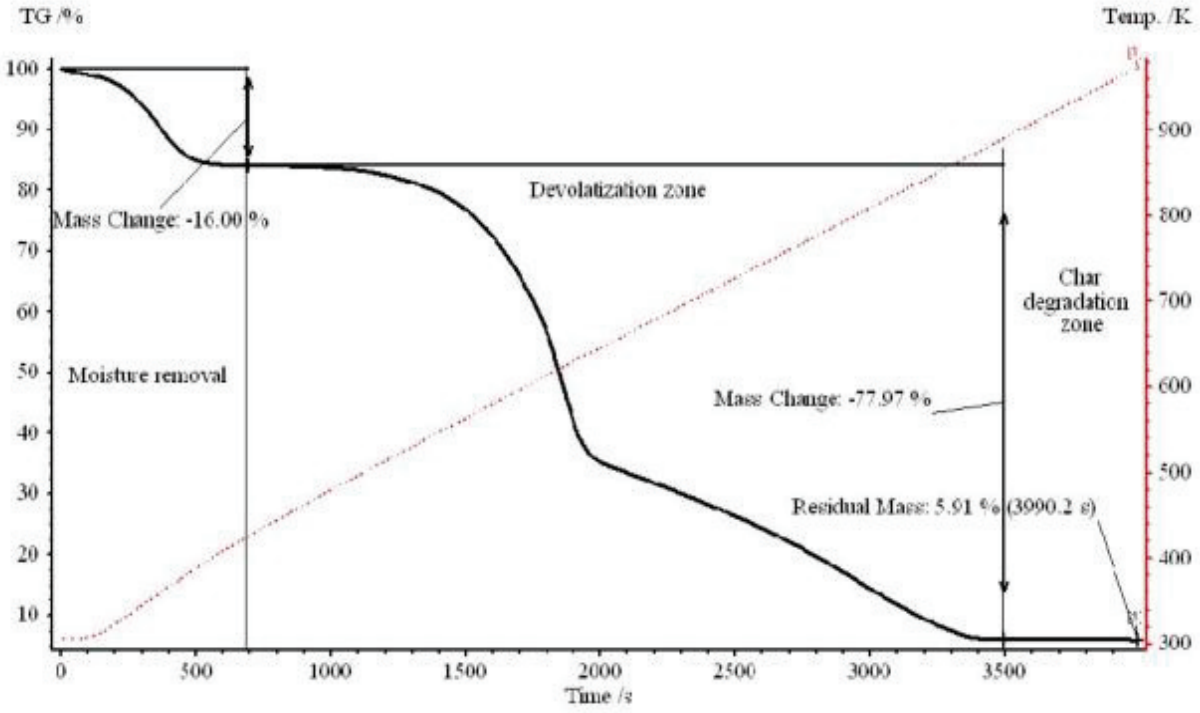

Figure 2. TG curve of pine sawdust at heating rate of 10 K/min

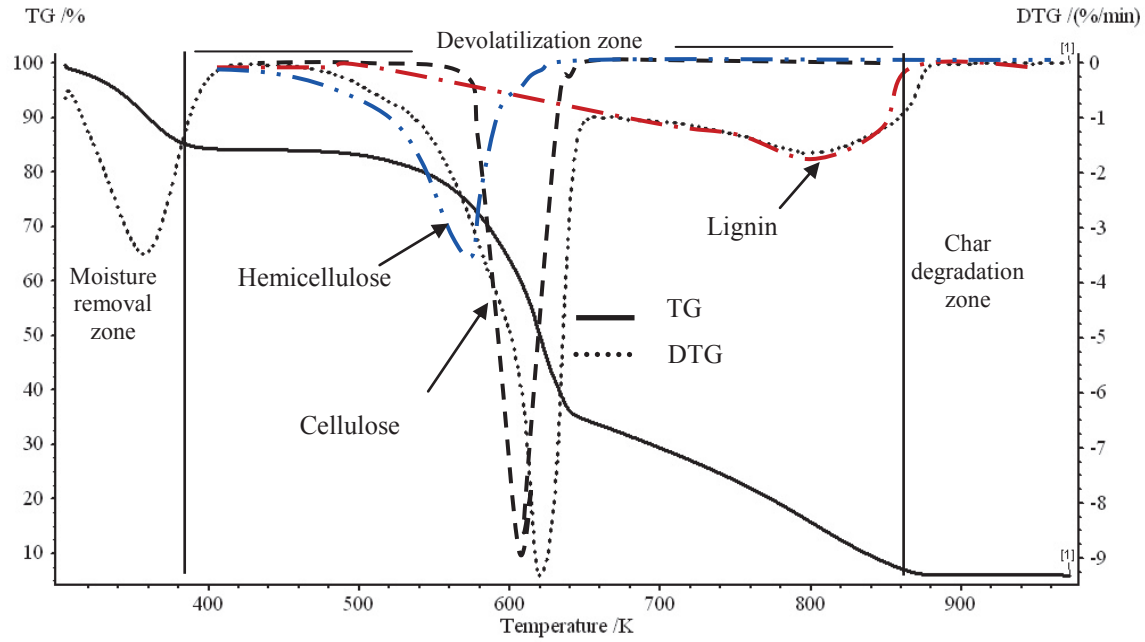

Figure 3. TG and DTG curves for pine sawdust at heating rate of 10 K/min

Figure 2 and 3 are the TG and derivative TG (DTG) profiles respectively showing the thermal degradation characteristics of pine sawdust at a heating rate of 10 K/min and demarked regions for moisture release, devolatilization and char degradation. The mass loss in the first stage takes place in the temperature range 303 K (30 °C) up to 420 K (147 °C), it was about 16% and it is associated with the evolution of sample moisture.

The moisture released during the thermo gravimetric analysis was a result of hygroscopicness of the individual biomass material. The hemicellulose degraded between 420 and 630 K, cellulose from 580 to 660 K, and finally lignin from 500 to 880 K. The major mass loss of nearly 80% is due to the devolatilization of the

hemicellulose, cellulose and lignin as shown in Figure 2. The Degradation temperatures of hemicellulose, cellulose and lignin are overlapping as shown in Figure 3. The observed two peaks are due to cellulose at 620 K and lignin degradation at 800 K. The hemicelluloses degradation is observed as a shoulder of the first peak at 590 K. The cellulose, hemicellulose and lignin shown in Figure 3, are known as pseudo-components, the cellulose is represented by dash black line, dash and double dots blue line is hemicellulose and dash with single dot red line is lignin.

Table 2. Kinetic parameters for pine sawdust

Parameter	Pine sawdust composite		
	Hemicelluloses	Cellulose	Lignin
Peak temperature (Tpeak, K)	590	620	800
Activation energy (Ea, kJ/mol)	259.9	457.6	90.0
Pre-exponential factor (A, s^{-1})	4.365x1023	3.33x1038	1.768x105
Reaction constant (k, s^{-1})	4.280	1.414	0.167

The values of activation energy (Ea) and pre-exponential factor (A) were calculated according to Kissinger's method and given in Table 2. The activation energy for cellulose is higher at about 460 kJ/mol, than that of hemicellulose at 260 kJ/mol and lignin at 90 kJ/mol. Hemicellulose decomposes at a lower temperature of 590 K and lignin at a temperature of 800 K.

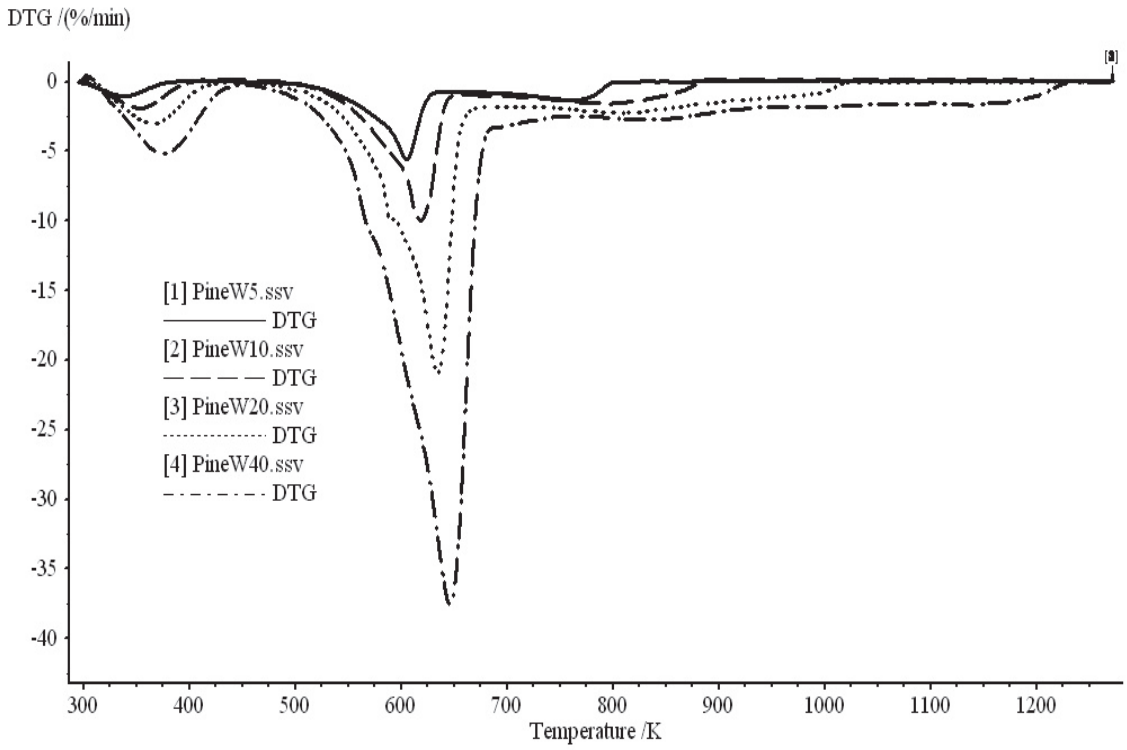

Figure 4. DTG curves of pine sawdust at different heating rates

Although the kinetic parameters of pseudo components describes the dissociation of pine sawdust, the total yield of the products during thermal degradation of pine sawdust can be estimated by global kinetic parameters due to the fact that it is vital to determine the global activation energy, pre-exponential factor and reaction constant. Figure 4 was obtained after degrading the pine sawdust at four different heating rates; 5, 10, 20 and 40 k/min. The estimated activation energy obtained was 143.741 kJ/mol and pre-exponential factor 6.205x1011 s^{-1}.

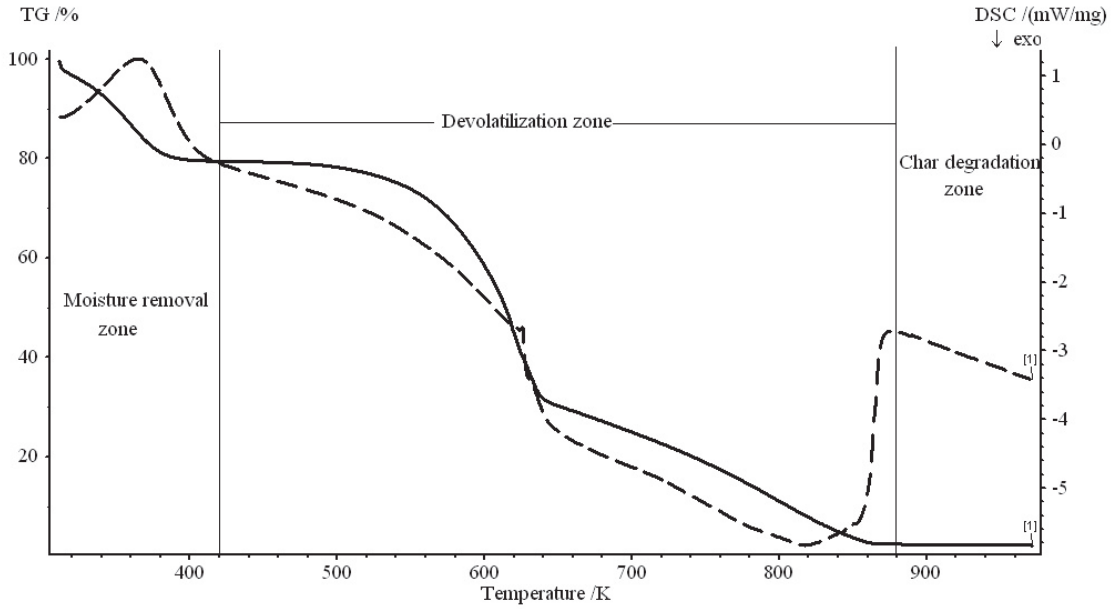

Figure 5. TG and DSC curves for pine sawdust at heating rate of 10 K/min

The DSC curve in Figure 5 shows the heat absorbed in the moisture release zone and heat released in the devolatilization zone during thermal degradation of pine sawdust. The sample absorbed 320.2 J/g at a temperature range from 303 to 420 K; this is due to evaporation of moisture. The heat releases of -4380 J/g was observed in the devolatilization zone between 420 and 880 K, this is due to the formation of hydrocarbons. The char degradation zones have negligible change of heat, since the rate of chemical reaction is very slow. The heat released was obtained, when pine sawdust heated under inert condition, while is expected to release 15.10 MJ/kg (15.10 kJ/g) under oxidation condition. Although the heat released by pine sawdust is almost half of that of coal, therefore the heat can be improved through torrefaction process (Biswas, 2012).

4. Conclusion

The thermal degradation characteristics study from the TG at a heating rate of 10 K/min showed that the volatile release region is most important part since about 81% of the material mass loss was experienced. The volatiles are most important during combustion of fuels.

Kinetic studies of pine sawdust materials by considering the pseudo-components established the kinetic parameters, the activation energy for cellulose is higher (about 460 kJ/mol) than that of hemicellulose (260 kJ/mol) and lignin (90 kJ/mol). Hemicellulose decomposes at a lower temperature of 590 K and lignin at a temperature of 800 K. These findings give background information for fuel product yield of bio-oil, gas and char.

The DSC revealed that the devolatilization zone is exothermic; this means that the pine sawdust can be used as a fuel under oxidation condition, since it can release energy. The energy content of pine sawdust is smaller than that of the coal due to high oxygen to carbon ratio. The energy content can be improved by converting the pine sawdust to either bio-oil, syngas or char through pyrolysis process. Although pine sawdust is a source of energy, it should be pre-treated to reduce ash content.

Nomenclature

A	Pre-exponential factor [s^{-1}]
DTG	Differential Thermogravimetry
DSC	Differential Scanning Calorimetry
E	Activation energy [kJ/mole]
f(α)	Conversion function[-]
H_m	Height of the peak [-]
K	Reaction constant [s^{-1}]

n	Reaction order
R	Universal gas constant [kJ/kmole-K]
T	Absolute temperature [K]
t	Time [s]
TG curve	Thermogravimetric curve
TGA	Thermogravimetric Analyzer
T_m	Peak temperature [℃ and K]
A	Degree of conversion [-]
β	Heating rate [K/min]

References

Biswas, A. (2012), "Thermochemical behaviour of pretreated biomass", Licentiate Thesis in Energy and Technology, KTH Industrial Engineering and Management, Stockholm, Sweden

Chmielniak, T. & Sciazko, M., (2003), Co-gasification of biomass nd coal for methanol synthesis, Applied Energy, 74, 393-403

Clarke, S. & Preto, F., (2011), Biomass Burn Characteristics, Factsheet, Ontario Ministry of Agriculture. www.omafra.gov.on.ca/english/engineer/facts/11-033.pdf

Criado, J. & Ortega, A., (1986), Non isothermal transformation kinetics: Remarks on Kissinger's method, Journal of Non Crystalline Solid, 87, 302-311

Kamwenda, G. & Mkeya, M., (2000), Status Report on Forest Based Industry and Products in Tanzania and Vision for the Future, Status of Forest Based Industry and Products in Tanzania and Vision for the Future Conference, March 28 – 29, 2000, Dar es Salaam, Tanzania

Kurkova, M., Klika, Z., Martinec, P. & Jaroslava, P., (2003), Composition of bituminous coal in dependence on environment and temperature of alteration. Bulletin of the Czech Geological Survey, 78 (1), 23–34

Lempp, P., (2013), "Biomass Co-firing Technology Brief", IEA-ETSAP and IRENA Technology Brief E21, www.irena.org/Publications

McKendry, P., (2002), Energy production from biomass (part 1): overview of biomass, Bioresource Technology, 83, 37–46

Miller, B. & Tillman D., (2008), "Combustion Engineering Issues for solid fuel systems", Academic Press is an imprint of Elsevier, 30 Corporate Drive, Suite 400, Barlington, MA 01803, USA. ISBN: 978-0-12-373611-6

Ngeleja, J. (2003), Potential role of forest/wood based cogeneration in Tanzania's power sector reform. In: Proceedings of the cooperative technology implementation plan for southern Africa workshop Dar es Salaam, 6-7

Parikh, J., Channiwala, S. & Ghosal G., (2007), A Correlation for Calculating Elemental Composition from Proximate Analysis of Biomass Materials, Fuel, 86, 1710-1719

Rose, S., Remedio, E. & Trossero, M. (2009), "Criteria and Indicator for Sustainable Wood Fuels. Case Studies from Brazil, Guyana, Nepal, Philippines and Tanzania", Food and Agriculture Organization of the United Nations, Rome, Italy

Sami, M. Annamalai, K. & Wooldridge, M., (2001), Co-firing of coal and biomass fuel blends, Progress in Energy and Combustion Science, 27, 171–214

Shao,Y., Wang, J., Preto, F., Zhu, J. & Xu, C., (2012), Ash Deposition in Biomass Combustion or Co-Firing for Power/Heat Generation, Energies, 5, 5171-5189, DOI: 10.3390/en 5125171

Stecher, K., Brosowski, A. & Thrän, D.(2013), "Biomass Potential in Africa", International Renewable Energy Agency, Abu Dhabi, United Arab Emirates

Tsamba, A., (2008), "Fundamental study of two selected tropical biomass for energy: Coconut and cashew nut shells", Doctoral Thesis, Energy and Furnace Technology, Stockholm, Sweden

Wilson, L., (2010), "Biomass Energy Systems and Resources in Tropical Tanzania", Licentiate Thesis in Furnance Technology Stockholm, Sweden. ISBN 978-91-7415-732-1

The IISTE is a pioneer in the Open-Access hosting service and academic event management. The aim of the firm is Accelerating Global Knowledge Sharing.

More information about the firm can be found on the homepage:
http://www.iiste.org

CALL FOR JOURNAL PAPERS

There are more than 30 peer-reviewed academic journals hosted under the hosting platform.

Prospective authors of journals can find the submission instruction on the following page: http://www.iiste.org/journals/ All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Paper version of the journals is also available upon request of readers and authors.

MORE RESOURCES

Book publication information: http://www.iiste.org/book/

Recent conferences: http://www.iiste.org/conference/

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library , NewJour, Google Scholar